Synthesis, Structural Characterization and Ligand Replacement Reactions of *Gem*-Dithiolato-Bridged Rhodium and Iridium Complexes

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Abstract

The reaction of *gem*-dithiol compounds $R_2C(SH)_2$ (R = Bn (benzyl), ^{i}Pr; R_2 = -$(CH_2)_4$-) with dinuclear rhodium or iridium complexes containing basic ligands such as $[M(\mu\text{-OH})(cod)]_2$ and $[M(\mu\text{-OMe})(cod)]_2$, or the mononuclear [M(acac)(cod)] (M = Rh, Ir, cod = 1,5-cyclooctadiene) in the presence of a external base, afforded the dinuclear complexes $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (**1**-**4**). The monodeprotonation of 1,1-dimercaptocyclopentane gave the mononuclear complex [Rh(HS_2Cptn)(cod)] (**5**) that is a precursor for the dinuclear compound $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**). Carbonylation of the diolefin compounds gave the complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ (**7**-**9**) which reacted with P-donor ligands to stereoselectively produce the *trans* isomer of the disubstituted complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$ (R' = Ph, Cy (cyclohexyl)) (**10**-**13**) and $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OR')_3\}_2]$ (R' = Me, Ph) (**14**-**15**). The substitution process in $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) by $P(OMe)_3$ has been studied by spectroscopic means and the full series of substituted complexes $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_{4-n}\{P(OR)_3\}_n]$ (n = 1, 4) has been identified in solution. The *cis* complex $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})]$ (**16**) was obtained by reaction of **7** with the diphosphine dppb (1,4-bis(diphenylphosphino)butane). The molecular structures of the diolefinic dinuclear complexes $[Rh_2(\mu\text{-}S_2CR_2)(cod)_2]$ (R = Bn (**1**), ^{i}Pr (**2**); R_2 = -$(CH_2)_4$- (**6**)) and that of the *cis*-complex **16** have been studied by X-ray diffraction.

Introduction

Transition metal-sulfur complexes have attracted considerable attention due to their significant relevance to biological and industrial processes.[1] In particular, thiolato derivatives of transition metals are of great importance in coordination chemistry and a large number of mono- and polynuclear compounds containing both simple and functionalized thiolato and dithiolato ligands have been synthesized and structurally characterized.[2] The long-standing interest in transition metal thiolate chemistry has been promoted from their relevance as model compounds of metal sites in metalloenzymes,[3] catalytic intermediates in the hydrodesulfurization process (HDS) in homogeneous phase,[4] and in the study of sulfur poisoning of solid catalysts.[5] However, the use of thiolate derivatives as building blocks for heteropolymetallic transition metal complexes[6] and supramolecular entities,[7] their potential application in transition-metal catalysis for the synthesis of organosulfur compounds[8] and their possible use as precursors for metal sulfides with important technological applications,[9] are additional aspects that have stimulated further developments in this field.

In contrast with the plentiful of transition metal complexes containing dithiolato ligands, the number of *gem*-dithiolato complexes, unlike those 1,1-ethylenedithiolato complexes and related unsaturated dithiolene ligands that exhibit planar geometry,[10] is very scarce. On the other hand, trialkylphosphonium-dithioformate complexes also have a four-membered dithiametallacyclobutane structural unit that results from the coordination of the two thiolato groups on the sp^3 carbon atom, however, these ligands are electronically very different due to the zwitterionic character of the $[S_2C(H)PR_3]^-$ ligand.[11] Surprisingly, all the known *gem*-dithiolato complexes have been obtained by indirect methods[12-19] which do not involve *gem*-dithiol compounds as reactants in spite that they were already described in the early sixties.[20] Rational synthetic routes to mono- and dinuclear complexes containing the simple methanedithiolato ligand $(S_2CH_2)^{2-}$ involve the alkylation of several bis-hydrosulfido, "$M_2(\mu\text{-}SH)_2$" (M = Mo, Re, Fe)[13] or bis-sulfido "$Pt_2(\mu\text{-}S)_2$" dinuclear complexes[14] by

dihalomethanes, generally in the presence of a base, or the insertion of carbon disulfide into M-H bonds (M = Cr, Mo, Re, Ru, Rh).[15] Other complexes with $(S_2CR_2)^{2-}$ ligands have been obtained, for example, by alkylation of dinuclear methanedithiolato complexes,[16] by the base induced double Michael addition of activated alkynes to dinuclear bis-hydrosulfido iron complexes,[17] or by addition of acetone to a mononuclear bis-hydrosulfido iridium compound in the presence of catalytic acid.[18] Interestingly, a variety of dirhenium *gem*-dithiolato complexes have been prepared by reaction of *cis*-$[Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-dppm})_2]$ with dihydrogen sulfide in the presence of aldehydes or ketones in acid media.[19]

Dinuclear d^8 transition-metal complexes with doubly bridged thiolates, $[M_2(\mu\text{-}SR)_2L_4]$, have recently attracted widespread interest regarding their electronic, structural and conformational properties.[21] However, dinuclear rhodium thiolato bridged complexes were already discovered to be effective catalysts in the hydroformylation of olefins under mild conditions in the early eighties.[22] Subsequent advances in rhodium thiolate chemistry were focused on the utilization of modified thiolato and dithiolato ligands, looking for the influence of a more rigid structure on the catalytic activity.[23] Furthermore, as chiral information can be introduced on the backbone of the dithiolato ligand, these dinuclear systems have found application in asymmetric hydroformylation, especially in combination with chiral diphosphines.[24] Interestingly, complexes with dithiolato ligands have also been used as synthons for the preparation of heterobimetallic complexes with catalytic activity.[25]

We have recently reported the straighforward synthesis of the complex $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ ($ChxnS_2^{2-}$ = 1,1-cyclohexanedithiolato) which is, to our knowledge, the first example of direct synthesis of a *gem*-dithiolato-bridged complex from a *gem*-dithiol compound.[26] This compound, as the bis-thiolato and dithiolato dinuclear counterparts, is an active catalyst precursor for the hydroformylation of olefins under mild conditions. We report herein the scope and limitations of this new synthetic methodology for the direct synthesis of diolefin dinuclear *gem*-dithiolato complexes $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (M = Rh, Ir) from several *gem*-dithiols ($R_2C(SH)_2$; R = Bn, ^{i}Pr; and R_2 = -

$(CH_2)_4$-). In addition, the reactivity of the rhodium complexes with carbon monoxide, the replacement reactions with several P-donor ligands and the comparison with the related thiolato dinuclear systems are also described.

Experimental Section

General. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Standard literature procedures were used to prepare the complexes $[Rh(\mu\text{-}OH)(cod)]_2$, $[M(\mu\text{-}OMe)(cod)]_2$ (M = Rh, Ir),[27] [M(acac)(cod)] (M = Rh, Ir),[28] $[Rh(acac)(CO)(PPh_3)]$[28a], $[Rh(acac)(CO)(PCy_3)]$.[29]

Physical Measurements. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.08, 121.47 and 75.46 MHz respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual resonances of the deuterated solvents (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external reference, respectively. Assignments in complex NMR spectra were done by simulation with the program gNMR© v 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. The initial choice of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure, a numerical assignment of the experimental frequencies was used. IR spectra were recorded on a Nicolet-IR 550 spectrometer. Elemental C, H and N analyses were performed with a Perkin-Elmer 2400 microanalyzer. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 Kv, 3-nitrobenzylic alcohol (NBA) was used as matrix.

Synthesis and Characterization of *gem*-Dithiol Compounds. 1,1-dimercaptocyclopentane, $Cptn(SH)_2$,[20a,b] 2,4-dimethyl-3,3-dimercaptopentane, $^iPr_2C(SH)_2$,[20c] and 1,3-diphenyl-2,2-

dimercaptopropane, $Bn_2C(SH)_2$,[20d] were prepared according to reported methods. Analytical and NMR data: **Cptn(SH)$_2$.** Anal. Calcd for $C_5H_{10}S_2$: C, 44.73; H, 7.51; S, 47.76. Found: C, 44.70; H, 7.48; S, 47.70. ^{1}H NMR ($CDCl_3$, 293 K) δ: 2.69 (s, 2H, SH), 2.06 (m, 4H, >CH_2), 1,81 (m, 4H, >CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 55.6, 48.1, 23.6 ($C(SH)_2$). **Bn$_2$C(SH)$_2$.** Anal. Calcd for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.62. Found: C, 69.14; H, 6.10; S, 24.50. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.33-7.28 (m, 10H, Ph), 3.22 (s, 4H, >CH_2), 2.36 (s, 2H, SH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 136.0, 131.5, 127.9, 127,4 (Ph), 56.8 ($C(SH)_2$), 52.8 (>CH_2). **^{i}Pr$_2$C(SH)$_2$.** Anal. Calcd for $C_7H_{16}S_2$: C, 51.16; H, 9.81; S, 39.02. Found: C, 51.10; H, 9,70; S, 38.91. ^{1}H NMR ($CDCl_3$, 293 K) δ: 2.08 (sept, 2H, $J_{H\text{-}H}$ = 7 Hz, CH, ^{i}Pr), 2.05 (s, 2H, SH), 1.07 (d, 12H, $J_{H\text{-}H}$ = 7 Hz, -CH_3, ^{i}Pr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 68.0 ($C(SH)_2$), 37.7 (CH), 18.2 (CH_3) (^{i}Pr).

Synthesis of the Complexes. [Rh$_2$(μ-S$_2$CBn$_2$)(cod)$_2$] (1). *Method A*. To a solution of [Rh(μ-OH)(cod)]$_2$ (0.500 g, 1.096 mmol) in CH_2Cl_2 (5 mL) was added 1,3-diphenyl-2,2-dimercaptopropane, $Bn_2C(SH)_2$, (0.312 g, 1.200 mmol) to give immediately an orange-red solution that was stirred for 15 min. The addition of EtOH (5 mL) afforded an orange suspension that was concentrated under vacuum to *ca* 5 mL and then filtered to give an orange microcrystalline solid which was washed with EtOH (2 x 3 mL) and dried under vacuum. Yield: 0.627 g (84 %). *Method B*. [Rh(μ-OMe)(cod)]$_2$ (0.100 g, 0.206 mmol) and $Bn_2C(SH)_2$ (0.054 g, 0.206 mmol) were reacted in CH_2Cl_2 (5 mL) to give immediately a red solution that was stirred for 30 min. The compound was isolated as an orange-brown microcrystalline solid following the procedure described above. Yield: 0.122 g (87 %). *Method C*. Triethylamine (120 μL, 0.652 mmol, ρ = 0.728 g mL^{-1}) and $Bn_2C(SH)_2$ (0.091 g, 0.350 mmol) were successively added to a solution of [Rh(acac)(cod)] (0.202 g, 0.650 mmol) in CH_2Cl_2 (5 mL) to give a red solution that was stirred for 15 min. Work-up as described above gave the compound as a red microcrystalline solid. Yield: 0.188 g (85%). Anal. Calcd for $C_{31}H_{38}S_2Rh_2$: C, 54.71; H, 5.63; S, 9.42. Found: C, 54.71; H, 5.90; S, 9.57. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.21 (m, 10H, Ph), 4.3 (m, 4H, =CH), 4.16 (m, 4H, =CH) (cod), 3.56 (s, 4H, >CH_2, Bn), 2.36 (m,

4H, >CH_2), 2.27 (m, 4H, >CH_2), 1.80 (m, 4H, >CH_2), 1.74 (m, 4H, >CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 137.8, 131.2, 127.6, 126.4 (Bn), 86.1 (CS_2), 79.9 (d, J_{Rh-C} = 12 Hz, =CH), 78.5 (d, J_{Rh-C} = 12 Hz, =CH) (cod), 60.9 (>CH_2, Bn), 30.6 (>CH_2, cod). MS (FAB$^+$, CH_2Cl_2, *m/z*): 680 (M^+, 25%), 572 (M^+ - cod, 15%), 464 (M^+ - 2cod, 22%).

[Rh_2(μ-$S_2C^iPr_2$)(cod)$_2$] (2). [Rh(μ-OH)(cod)]$_2$ (0.151 g, 0.331 mmol) and 2,4-dimethyl-3,3-dimercaptopentane, $^iPr_2C(SH)_2$, (52 μL, ρ ≅ 1 g mL^{-1}, 0.317 mmol) were reacted in CH_2Cl_2 (10 mL) at -78 ºC for 10 min. The solution was allowed to warm up to RT and stirred for 20 min. The resulting red-orange solution was concentrated under vacuum to about one half the volume and then EtOH (5 mL) was added to give a red-orange solid that was filtered, washed with EtOH (2 x 2 mL) and dried under vacuum. The solid was dissolved in an n-hexane/CH_2Cl_2 (2:1) mixture and then eluted through an alumina column (14 x 1.5 cm) to give an orange solution. Concentration of the solution afforded an orange microcrystalline solid that was filtered, washed with n-pentane (2 x 3 mL) and dried under vacuum. Yield: 0.151 g (78 %). Anal. Calcd for $C_{23}H_{38}S_2Rh_2$: C, 47.26; H, 6.55; S, 10.97. Found: C, 47.21; H, 6.40; S, 10.77. ^1H NMR ($CDCl_3$, 293 K) δ: 4.50 (m, 4H, =CH), 4.25 (m, 4H, =CH) (cod), 2.65 (sept, 2H, J_{H-H} = 6.9 Hz, CH, ^{i}Pr), 2.45 (m, 8H, >CH_2), 2.0 (m, 4H, >CH_2), 1.85 (m, 4H, >CH_2) (cod), 1.20 (d, 12H, J_{H-H} = 6.9 Hz, -CH_3, ^{i}Pr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 101.2 (CS_2), 79.5 (d, J_{Rh-C} = 11.5 Hz, =CH), 78.6 (d, J_{Rh-C} = 12.4 Hz, =CH) (cod), 46.5 (CH, ^{i}Pr), 31.6 and 31.1 (>CH_2) (cod), 20.1 (-CH_3, ^{i}Pr). MS (FAB$^+$, CH_2Cl_2, *m/z*): 584 (M^+, 100%).

[Ir_2(μ-S_2CBn_2)(cod)$_2$] (3). [Ir(acac)(cod)] (0.104 g, 0.260 mmol) and $Bn_2C(SH)_2$ (0.040 g, 0.153 mmol) were reacted in CH_2Cl_2 (5 mL) for 15 min to give a dark-red suspension. The suspension was concentrated under vacuum to about one half the volume and then MeOH (3 mL) was added to complete the precipitation. The compound was isolated by filtration, washed with MeOH (2 x 2 mL) and dried under vacuum. Yield: 0.099 g (88 %). Anal. Calcd for $C_{31}H_{38}S_2Ir_2$: C, 43.34; H, 4.46; S, 7.46. Found: C, 43.29; H, 4.36; S, 6.61. ^1H NMR ($CDCl_3$, 293 K) δ: 7.23 (m, 10H, Ph), 4.04 (m, 2H, =CH), 3.81 (m, 2H, =CH) (cod), 3.51 (s, 4H, >CH_2, Bn), 2.09 (m, 8H, >CH_2), 1.66 (m, 4H, >CH_2),

1.27 (m, 4H, >CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 137.7, 131.2, 127.8, 126.6 (Bn), 95.1 (CS_2), 66.2 (=CH, cod), 63.0 (>CH_2, Bn), 62.9 (=CH), 31.8 and 31.6 (>CH_2, cod). MS (FAB^+, CH_2Cl_2, *m/z*): 860 (M^+, 40%), 661 (M^+ - cod - Bn, 30%).

[Ir_2(μ-$S_2C^iPr_2$)(cod)$_2$] (4). [Ir(μ-OMe)(cod)]$_2$ (0.126 g, 0.190 mmol) and $^iPr_2C(SH)_2$ (29 μL, ρ ≅ 1 g mL^{-1}, 0.177 mmol) were reacted in CH_2Cl_2 (10 mL) at -78 ºC for 10 min. The compound was isolated as a dark red solid following the procedure described for compound **2**. The crude compound was dissolved in a n-hexane/CH_2Cl_2 (3:1) mixture and then eluted through an alumina column (14 x 1.5 cm) to give a violet solution. Concentration of the solution afforded a purple microcrystalline solid that was filtered, washed with n-pentane (2 x 3 mL) and dried under vacuum. Yield: 0.110 g (76%). Anal. Calcd for $C_{23}H_{38}S_2Ir_2$: C, 36.20; H, 5.02; S, 8.40. Found: C, 36.00; H, 4.73; S, 8.83. ^1H NMR ($CDCl_3$, 293 K) δ: 4.26 (m, 4H, =CH), 3.92 (m, 4H, =CH) (cod), 2.48 (sept, 2H, CH, $J_{H\text{-}H}$ = 6.9 Hz, ^iPr), 2.28 (m, 4H, >CH_2), 2.16 (m, 4H, >CH_2), 1.87 (m, 4H, >CH_2), 1.41 (m, 4H, >CH_2) (cod), 0.98 (d, 12H, -CH_3, $J_{H\text{-}H}$ = 6.9 Hz, ^iPr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 110.4 (CS_2), 65.7 and 63.2 (=CH, cod), 50.6 (CH, ^iPr), 32.6 and 31.9 (>CH_2, cod), 19.9 (-CH_3, ^iPr). MS (FAB^+, CH_2Cl_2, *m/z*): 762 (M^+, 100%), 613 (M^+ - cod - ^iPr, 24%).

[Rh(HS_2Cptn)(cod)] (5). To a solution of [Rh(acac)(cod)] (0.171 g, 0.550 mmol) in CH_2Cl_2 (10 mL) was added 1,1-dimercaptocyclopentane, Cptn$(SH)_2$, (77 μL, 0.550 mmol, ρ = 0.95 g mL^{-1}) to give immediately a dark red solution that was stirred for 15 min. The solution was concentrated under vacuum to *ca*. 5 mL and then MeOH (5 mL) was added to give a dark red suspension. The suspension was further concentrated and then diethyl ether (5 mL) was added to complete the precipitation. The suspension was filtered and then recrystallized from CH_2Cl_2/diethyl ether to give the compound as a dark red solid. Yield: 0.128 g (68 %). Anal. Calcd for $C_{13}H_{21}S_2Rh$: C, 45.34; H, 6.15; S, 18.62. Found: C, 45.30; H, 5.95; S, 18.13. ^1H NMR ($CDCl_3$, 293 K) δ: 4.18 (m, 4H, =CH) (cod), 2.39 (m, 5H, >CH_2, cod and SH), 1.93 (br, 4H, >CH_2) (cod), 1.82 (m, 4H, >CH_2), 1.64 (m, 4H, >CH_2) (Cptn). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 81.7 (d, $J_{Rh\text{-}C}$ = 11 Hz, =CH, cod), 66.8 (C^1),

48.5 (C^2 and C^5) (Cptn), 31.6 (>CH_2, cod), 23.8 (C^3 and C^4, Cptn). MS (FAB^+, CH_2Cl_2, *m/z*): 554 (M^+ + Rh(cod) - H, 89%), 343 (M^+ - H, 67%).

[Rh_2(μ-S_2Cptn)(cod)$_2$] (6). [Rh(μ-OH)(cod)]$_2$ (0.350 g, 0.767 mmol) and Cptn(SH)$_2$, (108 μL, 0.767 mmol, ρ = 0.95 g mL^{-1}) were reacted in CH_2Cl_2 (10 mL) at RT for 10 min. The compound was isolated as a dark red solid following the procedure described for compound **1**. The crude compound was dissolved in CH_2Cl_2 and then eluted through an alumina column (12 x 1.5 cm) with n-hexane/dichloromehane (2:1) to give an orange solution. Concentration of the solution afforded an orange microcrystalline solid that was filtered, washed with n-pentane (2 x 3 mL) and dried under vacuum. Yield: 0.263 g (62 %). Anal. Calcd for $C_{21}H_{32}S_2Rh_2$: C, 45.49; H, 5.82; S, 11.56. Found: C, 45.61; H, 5.69; S, 11.23. ^{1}H NMR (C_6D_6, 293 K) δ: 4.85 (m, 4H, =CH), 4.44 (m, 4H, =CH) (cod), 2.54 (m, 4H, >CH_2, Cptn), 2.46 (m, 8H, >CH_2), 2.00 (m, 4H, >CH_2), 1.85 (m, 4H, >CH_2) (cod), 1.70 (m, 4H, >CH_2, Cptn). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) d: 79.9 (d, $J_{Rh\text{-}C}$ = 11 Hz, =CH), 78.9 (d, $J_{Rh\text{-}C}$ = 12 Hz, =CH) (cod), 81.9 (C^1), 60.0 (C^2 and C^5) ($CptnS_2$), 31.5 and 31.1 (>CH_2, cod), 25.0 (C^3 and C^4, Cptn). MS (FAB^+, CH_2Cl_2, *m/z*): 554 (M^+, 100%), 446 (M^+ - cod, 45%), 338 (M^+ - 2cod, 32%).

[Rh_2(μ-S_2CBn_2)(CO)$_4$] (7). Carbon monoxide was bubbled through an orange solution of [Rh_2(μ-S_2CBn_2)(cod)$_2$] (**1**) (0.100 g, 0.147 mmol) in CH_2Cl_2 (5 mL) for 10 min to give a pale red solution. n-Hexane (10 mL) was added and the volume of the solution reduced by continuous bubbling of carbon monoxide until a red solid precipitated. Addition of n-hexane (3 mL) and concentration by bubbling led to further precipitation. The compound was isolated by filtration, washed with n-hexane (2×3 mL) and dried under vacuum. Yield: 0.078 g (92 %). Anal. Calcd for $C_{19}H_{14}O_4S_2Rh_2$: C, 39.60; H, 2.45; S, 11.13. Found. C, 39.90; H, 2.63; S, 11.09. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.45 (m, 8H), 7.28 (m, 2H), 3.31 (s, 4H, >CH_2) (S_2CBn_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K) δ: 184.4 (d, $J_{Rh\text{-}C}$ = 72 Hz, CO), 136.9, 132.1, 128.3, 127.8, (Bn), 95.4 (CS_2), 60.6 (>CH_2, Ph). MS (FAB^+, CH_2Cl_2, *m/z*): 576 (M^+, 70%); 548 (M^+ - CO, 95%), 520 (M^+ - 2CO, 70%), 492 (M^+ - 3CO, 85%), 464 (M^+ - 4CO, 100%), 430 (M^+ - 2CO - Bn, 80%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2078 (m), 2054 (s), 2010 (s).

[$Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(PPh_3)_2$] (10). *Method A*. To a solution of [Rh(acac)(CO)(PPh_3)] (0.103 g, 0.209 mmol) in CH_2Cl_2 (10 mL) was added $Bn_2C(SH)_2$ (0.027 g, 0.105 mmol) to give a red solution that was stirred for 15 min. The solution was concentrated under vacuum to about one half the volume and then MeOH (6 mL) was added to afford an orange solid that was filtered, washed with MeOH (2 x 3 mL) and dried under vacuum. Yield: 0.101 g (92 %). *Method B*. To a solution of compound [$Rh_2(\mu\text{-}S_2CBn_2)(CO)_4$] (**7**), prepared in situ by carbonylation of [$Rh_2(\mu\text{-}S_2CBn_2)(cod)_2$] **(1)** (0.100 g, 0.147 mmol) in CH_2Cl_2 (10 mL) for 15 min was added solid PPh_3 (0.077 g, 0.295 mmol) to give an orange solution with evolution of carbon monoxide. The solution was stirred for 10 min and then MeOH (10 mL) was added to give a red suspension. Concentration of the suspension to about one half the volume led to further precipitation. Filtration and washing with MeOH (3 × 3 mL) following by drying under vacuum gave the product as an orange-red solid. Yield: 0.138 g (90 %). Anal. Calcd for $C_{53}H_{44}O_2P_2S_2Rh_2$: C, 60.93; H, 4.24; S, 6.14. Found: C, 60.43; H, 4.44; S: 6.04. ^{1}H NMR (C_6D_6, 293 K) δ: 7.6 (m, 12H), 7.3 (m, 18H) (PPh_3), 7.0 (m, 10H, Ph), 3.50 (AB q: $\delta_A = 3.98$, $\delta_B = 3.3$, $J_{AB} = 14.1$ Hz, 4H, $>CH_2$, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6; 293 K) δ: 192.5 (dd, $J_{Rh\text{-}C} = 76$ Hz, $^2J_{P\text{-}C} = 18$ Hz, CO), 138.7 (Ph), 135.8 (d, $J_{P\text{-}C} = 72$ Hz), 134.8 (d, $J_{P\text{-}C} = 12$ Hz) (PPh_3), 131.8 (Ph), 130.5 (PPh_3), 128.9 (d, $J_{P\text{-}C} = 12$ Hz) (PPh_3), 127.1 (Ph), 89.1 (CS_2), 61.9 ($>CH_2$, Bn). MS (FAB$^+$, CH_2Cl_2, *m/z*): 1044 (M^+, 100%), 1016 (M^+ - CO, 35%), 988 (M^+ - 2CO, 11%), 754 (M^+ - CO - PPh_3, 36%). IR (toluene, cm^{-1}): ν(CO), 1967 (s).

[$Rh_2(\mu\text{-}S_2C^iPr_2)(CO)_2(PPh_3)_2$] (11). Carbon monoxide was bubbled through a solution of [$Rh_2(\mu\text{-}S_2C^iPr_2)(cod)_2$] **(2)** (0.086 g, 0.147 mmol) in CH_2Cl_2 (10 mL) to give a yellow-brown solution of the compound [$Rh_2(\mu\text{-}S_2C^iPr_2)(CO)_4$] (**8**) in 15 min. Further reaction with PPh_3 (0.077 g, 0.294 mmol) gave a deep red solution with evolution of carbon monoxide. Work-up as described above for compound **10** (method B) gave the compound as a red solid. Yield: 0.120 g (93 %). Anal. Calcd for $C_{45}H_{44}O_2P_2S_2Rh_2$: C, 56.97; H, 4.67; S, 6.76. Found: C, 56.56; H, 4.73; S, 6.75. ^{1}H NMR (C_6D_6, 293 K) δ: 8.11 (m, 12H), 7.32-7.18 (m, 18H) (PPh_3), 3.07 (m, 2H, CH), 1.19 (d, $J_{H\text{-}H} = 6.9$ Hz, $-CH_3$),

1.13 (d, J_{H-H} = 6.9 Hz, -CH_3) (^{i}Pr). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K) δ: 191.7 (dd, J_{Rh-C} = 75 Hz, $^2J_{P-C}$ = 17 Hz, CO), 135.2 (d, J_{P-C} = 44 Hz), 133.5 (d, J_{P-C} = 12 Hz), 129.6, 128.2 (d, J_{P-C} = 5 Hz) (PPh_3), 102.3 (CS_2), 47.6 (CH), 19.2 and 19.1(-CH_3) (^{i}Pr). MS (FAB$^+$, CH_2Cl_2, *m/z*): 948 (M^+, 100%); 920 (M^+ - CO, 50%); 890(M^+ - 2CO, 40%); 686 (M^+ - PPh_3, 35%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1956 (s).

[Rh_2(μ-S_2Cptn)(CO)$_2$(PPh_3)$_2$] (12). [Rh(acac)(CO)(PPh_3)] (0.065 g, 0.132 mmol) and Cptn$(SH)_2$ (10.7 μL, 0.075 mmol, ρ = 0.95 g mL^{-1}) were reacted in CH_2Cl_2 (10 ml) for 15 min to give an orange solution. The compound was isolated as an orange solid following the procedure described for compound **10** (method A). Yield: 0.049 g (81 %). Anal. Calcd for $C_{43}H_{38}O_2P_2S_2Rh_2$: C, 56.22; H, 4.17; S, 6.98. Found: C, 56.00; H, 4.16; S: 7.03. ^1H NMR ($CDCl_3$, 293 K) δ: 7.77-7.69 (m, 12H), 7.42-7.33 (m, 18H) (PPh_3), 2.19 (m, 4H, >CH_2), 1.57 (m, 4H, >CH_2) (Cptn). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 191.4 (dd, J_{Rh-C} = 76 Hz, $^2J_{P-C}$ = 17 Hz, CO), 134.8 (d, J_{P-C} = 46 Hz), 133.9 (d, J_{P-C} = 12 Hz), 129.8 (s), 128.1 (d, J_{P-C} = 12 Hz) (PPh_3), 84.3 (C^1), 60.0 (C^2 and C^5), 24.5 (C^3 and C^5) (Cptn). MS (FAB$^+$, CH_2Cl_2, *m/z*): 918 (M^+, 82%), 890 (M^+ - CO, 55%). IR (toluene, cm^{-1}): ν(CO), 1972 (s).

[Rh_2(μ-S_2CBn_2)(CO)$_2$(PCy_3)$_2$] (13). [Rh(acac)(CO)(PCy_3)] (0.103 g, 0.202 mmol) and $Bn_2C(SH)_2$ (0.026 g, 0.101 mmol) were reacted in CH_2Cl_2 (10 mL) for 15 min to give a pale orange solution that was stirred for 15 min. The compound was isolated as a yellow solid following the procedure described for compound **10** (method A). Yield: 0.089 g (82 %). Anal. Calcd for $C_{53}H_{80}O_2P_2S_2Rh_2$: C, 58.88; H, 7.46; S, 5.93. Found: C, 58.35; H, 7.22; S, 6.02. ^1H NMR ($CDCl_3$, 293 K) δ: 7.20 (m, 10H, Bn), 3.96 (AB q, δ_A = 4.02, δ_B = 3.88, J_{AB} = 14.85 Hz, 4H, >CH_2, Bn), 2.04 (m, 18 H), 1.75 (m, 30 H), 1.23 (m, 18 H) (PCy_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ: 192.1 (dd, J_{Rh-C} = 76.9 Hz, $^2J_{P-C}$ = 17.5 Hz, CO), 138.6, 130.8, 128.2, 126.7 (Bn), 86.2 (CS_2), 62.0 (>CH_2, Bn), 37.0 (d, J_{P-C} = 22 Hz, -CHP), 30.7, 28.1 (d, J_{P-C} = 12.4 Hz), 26.9 (>CH_2, PCy_3). MS (FAB$^+$, CH_2Cl_2, *m/z*): 1080 (M^+, 17%), 1052 (M^+ - CO, 20%), 1024 (M^+ - 2CO, 15%), 744 (M^+ - 2CO - PCy_3, 30%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1942 (s).

[$Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OMe)_3\}_2$] (14). To a solution of [$Rh_2(\mu\text{-}S_2CBn_2)(CO)_4$] **(7)** (0.024 g, 0.042 mmol) in CH_2Cl_2 (5 mL) at RT was added $P(OMe)_3$ (10 μL, 0.084 mmol, ρ = 1.05 g mL^{-1}, 98%) to give a yellow solution with evolution of carbon monoxide. The solution was stirred for 10 min and then n-hexane (5 ml) was added. The solvent was slowly eliminated under vacuum and the resulting thick solid washed with n-hexane (3x3 mL) to give a light orange solid that was filtered and dried under vacuum. Yield: 0.029 g (91 %). Anal. Calcd for $C_{23}H_{32}O_8P_2S_2Rh_2$: C, 35.95; H, 4.20; S, 8.34. Found. C, 36.15; H, 4.18; S, 8.12. ^{1}H NMR (C_6D_6, 293 K) δ: 7.54 (d, 4H), 7.27 (m, 4H), 7.19 (d, 2H) (Bn), 3.79 (AB q: $\delta_A = 4.08$, $\delta_B = 3.50$, $J_{AB} = 13.35$ Hz, 4H, $>CH_2$, Bn), 3.58 (d, $^2J_{C\text{-}P} = 12$ Hz, -OMe). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K) δ: 190.24 (dd, $J_{Rh\text{-}C} = 74$ Hz, $^2J_{P\text{-}C} = 24$ Hz, CO), 137.98, 131.59, 128.59, 127.20 (Bn), 90.42 (CS_2), 62.56 ($>CH_2$, Bn), 51.70 (OMe). MS (FAB^+, CH_2Cl_2, *m/z*): 768 (M^+, 32%), 712 (M^+ - 2CO, 100%), 616 (M^+ - CO - $P(OMe)_3$, 33%), 588 (M^+ - 2CO - $P(OMe)_3$, 45%), 464 (M^+ - 2CO - $2P(OMe)_3$, 25%). IR (toluene, cm^{-1}): ν(CO), 1986 (s).

[$Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OPh)_3\}_2$] (15). [$Rh_2(\mu\text{-}S_2CBn_2)(CO)_4$] **(7)** (0.020 g, 0.035 mmol) and $P(OPh)_3$ (19 μL, 0.070 mmol, ρ = 1.184 g mL^{-1}, 97%) were reacted in CH_2Cl_2 (5 ml) at RT to give a yellow solution with evolution of carbon monoxide. Work-up as described above gave the compound as a yellow solid. Yield: 0.035 g (88%). Anal. Calcd for $C_{53}H_{44}O_8P_2S_2Rh_2$: C, 55.80; H, 3.89; S, 5.62. Found: C, 55.68; H, 4.02; S, 5.55. ^{1}H NMR (C_6D_6, 293 K) δ: 7.71 (d, 12H, OPh), 7.51-7.33 (m, 10H, Bn), 7.27 (m, 12H), 7.06 (m, 6H) (OPh), 3.68 (AB q: $\delta_A = 3.68$, $\delta_B = 3.48$, $J_{AB} = 14.4$ Hz, 4H, $>CH_2$, Bn). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K) δ: 189.2 (d, $J_{Rh\text{-}C} = 74$ Hz, $^2J_{P\text{-}C} = 24$ Hz, CO), 152.4 (d, $J = 6$ Hz, OPh), 137.6, 131.7 (Bn), 130.2 (OPh), 128.5, 127.3 (Bn), 125.5, 121.9 (OPh), 89.1 (CS_2), 61.8 ($>CH_2$, Bn). MS (FAB^+, CH_2Cl_2, *m/z*): 1140 (M^+, 20%), 1112 (M^+ - CO, 30%), 1084 (M^+ - 2CO, 45%), 802 (M^+ - $P(OPh)_3$ -CO, 35%), 774 (M^+ - $P(OPh)_3$ -2CO, 85%). IR (toluene, cm^{-1}): ν(CO), 1994 (s).

[$Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})$] (16). To a solution of **7**, prepared in situ by carbonylation of [$Rh_2(\mu\text{-}S_2CBn_2)(cod)_2$] **(1)** (0.059 g, 0.087 mmol) in CH_2Cl_2 (10 mL) was added solid dppb (0.036 g, 0.087 mmol) to give a yellow solution with evolution of carbon monoxide. The solution was stirred for 10 min and then concentrated under vacuum to about one half the volume. The addition of MeOH (5 mL) gave the compound as a yellow solid that was filtered, washed with cold MeOH (3×3 mL) and dried under vacuum. Yield: 0.072 g (87 %). Anal. Calcd for $C_{45}H_{42}O_2P_2S_2Rh_2$: C, 57.09; H, 4.47; S, 6.77. Found: C, 56.94; H, 4,35; S, 6.65. ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.80 (m, 4H), 7.67 (m, 4H), 7.64-7.00 (m, 14H), 7.04 (m, 8H) (Bn and dppb), 3.56 (AB q, $\delta_A = 3.59$, $\delta_B = 3.54$, $J_{AB} = 14.10$ Hz, 4H, $>CH_2$, Bn), 2.46 (m, 4H), 2.20 (m, 2H), 1.40 (m, 2H) ($>CH_2$, dppb). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ: 32.25 (d, $J_{Rh\text{-}P} = 157$ Hz). MS (FAB^+, CH_2Cl_2, *m/z*): 946 (M^+, 95%), 918 (M^+ - CO, 26%), 890 (M^+ - 2CO, 72%). IR (toluene, cm^{-1}): ν(CO), 1980 (s).

Crystal Structure Determination of [$Rh_2(\mu\text{-}S_2CBn_2)(cod)_2$] (1), [$Rh_2(\mu\text{-}S_2C^iPr_2)(cod)_2$] (2), [$Rh_2(\mu\text{-}S_2Cptn)(cod)_2$] (6) and [$Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})$] (16). Suitable crystals for X-ray diffraction of compounds **1**, **2**, **6** and **16** were obtained by slow diffusion of n-hexane into CH_2Cl_2 solutions of the complexes at 258 K. A summary of crystal data and refinement parameters for the structural analyses is given in Table 6. The crystals used in the analyses were glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) at low temperature (173 K (**1**) or 100(1) K (**2**, **6** and **16**)). Cell constants were obtained from the least-squares refinement of three-dimensional centroids (3185 refl., $4.5 \leq 2\theta \leq 29.3°$ for **1**; 6234, 9863 or 19904 ref., $4.5 \leq 2\theta \leq 56.6°$ for **2**, **6** or **16** respectively). Data were measured through the use of CCD recording of narrow ω rotation frames (0.3° each). All data were integrated with the Bruker SAINT program[30] which includes Lorentz and polarization corrections. Absorption correction was applied by using the SADABS routine.[31]

The structures were solved by Patterson methods, completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97)[32] with initial isotropic, but subsequent anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms in **1** were included in the model from calculated or observed (olefinic hydrogens) positions, but were refined with riding positional and displacement parameters. In the case of **2**, **6** and **16**, hydrogen atoms were obtained from difference Fourier maps, and refined as free isotropic atoms. Atomic scattering factors were used as implemented in the program.[32]

Results

Synthesis and Characterization of Diolefin *gem*-Dithiolato-bridged Rhodium and Iridium Dinuclear Compounds. The synthesis of *gem*-dithiolato-bridged dinuclear complexes can be accomplished directly from *gem*-dithiol compounds using standard mono- or dinuclear compounds containing basic ligands. Thus, reaction of $[Rh(\mu\text{-}OH)(cod)]_2$ with 1,3-diphenyl-2,2-dimercaptopropane, $Bn_2C(SH)_2$, in dichloromethane at room temperature gave a red-orange solution of the compound $[Rh_2(\mu\text{-}S_2CBn_2)(cod)_2]$ (**1**) which was isolated as an orange-red microcrystalline solid in good yield. The synthesis of compound **1** can be also carried out in similar yields starting from $[Rh(\mu\text{-}OMe)(cod)]_2$ or [Rh(acac)(cod)] (1:2 molar ratio), although addition of an external base (NEt_3) is convenient for the later compound in order to drive the reaction to completion. The related iridium dinuclear compound $[Ir_2(\mu\text{-}S_2CBn_2)(cod)_2]$ (**3**) was obtained as a purple microcrystalline solid in good yield from $Bn_2C(SH)_2$ and [Ir(acac)(cod)] (1:2 molar ratio) although without the need of an external base, probably due to the low solubility of the complex in the reaction media (Scheme 1).

The synthetic flexibility observed in the case of $Bn_2C(SH)_2$ is not completely applicable to the preparation of dinuclear complexes with 2,4-dimethyl-3,3-dimercaptopentane, $^{i}Pr_2C(SH)_2$, as the synthesis is generally problematic due to side reactions. Thus, following a similar synthetic protocol, reaction of $^{i}Pr_2C(SH)_2$ with [Rh(acac)(cod)] (1:2 molar ratio) in dichloromethane gave a deep red

solution from which the trinuclear hydride cluster $[Rh_3(\mu_3\text{-}S)_2(\mu\text{-}H)(cod)_3]$[33a] was isolated in 55% yield (Scheme 2). It is known that some *gem*-dithiol compounds are transformed into the corresponding thione by $SH_2(g)$ elimination.[34] Thus, the formation of the cluster is probably driven by the $SH_2(g)$ formed by decomposition of $^{i}Pr_2C(SH)_2$ mediated by [Rh(acac)(cod)]. This interpretation is sustained together by the detection in the reaction media of the thione $^{i}Pr_2C{=}S$ (GC/MS evidence) and by the clean formation of $[Rh_3(\mu_3\text{-}S)_2(\mu\text{-}H)(cod)_3]$ by reaction of [Rh(acac)(cod)] with $SH_2(g)$.

Nevertheless, the formation of the hydride clusters $[M_3(\mu_3\text{-}S)_2(\mu\text{-}H)(cod)_3]$ (M = Rh, Ir)[33] is minimized by using rhodium and iridium dinuclear compounds as starting materials. Thus, reaction of $^{i}Pr_2C(SH)_2$ with $[Rh(\mu\text{-}OH)(cod)]_2$ or $[Ir(\mu\text{-}OMe)(cod)]_2$ afforded the compounds $[Rh_2(\mu\text{-}S_2C^{i}Pr_2)(cod)_2]$ (**2**) and $[Ir_2(\mu\text{-}S_2C^{i}Pr_2)(cod)_2]$ (**4**) which were isolated as orange and purple microcrystalline solids in 76% yield after chromatography purification to remove the hydride clusters (Scheme 1).

Compounds **1**-**4** have been fully characterized by elemental analysis, FAB mass spectra and multinuclear NMR spectroscopy. In addition, the structures of compounds **1** and **2** have been determined by X-ray diffraction methods (Figures **1** and **2**) showing the bridging and chelating coordination mode (1:2k^2S, 1:2k^2S') of the *gem*-dithiolato ligands. The ^1H NMR of the compounds showed no resonances attributable to SH protons indicating the complete deprotonation of the *gem*-dithiol compounds upon formation of the complexes. The ^1H and $^{13}C\{^1H\}$ NMR showed rigid structures that are in agreement with the dinuclear structures of C_{2v} symmetry found in the solid. In particular, the ^1H NMR spectra showed the expected two sharp resonances for the =CH protons and four sharp multiplets for the $>CH_2$ protons as a consequence of the differentiation between the two groups of *exo* and *endo* protons of the equivalent cod ligands. In accordance with the chemical equivalence of both benzyl and isopropyl fragments of the *gem*-dithiolato ligands in the structures, the benzylic and isopropylic protons were observed as a sharp singlet in compounds **1** and **3**, and as

the expected septuplet and doublet (1:6 ratio, $^{3}J_{H\text{-}H} \approx 6.9$ Hz) in compounds **2** and **4**, respectively. The formation of the dimetallic core in complexes **1**-**4** strongly influences the chemical shift of the resonance of the geminal carbon atoms of the bridging *gem*-dithiolato ligands in the $^{13}C\{^{1}H\}$ NMR spectra. This resonance is shifted to higher frequencies, compared to the free *gem*-dithiols, by about 30 ppm in the rhodium complexes (**1** and **2**) and 40 ppm in the iridium ones (**3** and **4**), and reflects the effect of the ligand coordination to the metal centers.

Stepwise Formation of Dinuclear *gem*-Dithiolato-bridged Compounds. The monitoring of the reaction of [Rh(acac)(cod)] with $Bn_2C(SH)_2$ in $CDCl_3$ by ^{1}H NMR spectroscopy showed the exclusive formation of the dinuclear compound $[Rh_2(\mu\text{-}S_2CBn_2)(cod)_2]$ (**1**) independently of the utilized molar ratio (1:1 or 2:1) as a consequence of the simultaneous deprotonation of both –SH groups of $Bn_2C(SH)_2$. In sharp contrast, we have observed that in some cases the deprotonation of the *gem*-dithiol compounds by rhodium complexes can be carried out sequentially.

The reaction of 1,1-dimercaptopentane, $Cptn(SH)_2$, with [Rh(acac)(cod)] (1:2 molar ratio) and NEt_3 in dichlorometane gave a brown solution from which a brown solid was isolated. The ^{1}H NMR analysis of this solid in $CDCl_3$ evidenced the formation of the dinuclear compound $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**) together with the mononuclear $[Rh(HS_2Cptn)(cod)]$ (**5**) which was present in, roughly, 20%. However, when the reaction was conducted in a 1:1 molar ratio without NEt_3 under the same conditions, the composition of the mixture was reversed and the resulting dark red solution showed almost an 85% of the mononuclear species (Scheme 3). In fact, the mononuclear compound $[Rh(HS_2Cptn)(cod)]$ (**5**) was isolated as a dark red solid in 68% yield after recrystallization of the crude obtained following this procedure. The dinuclear compound $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**) has been obtained as an orange solid in 62% yield from $[Rh(\mu\text{-}OH)(cod)]_2$ and $Cptn(SH)_2$ after purification by chromatography to remove **5** that is formed in trace amounts. Interestingly, the deprotonation of $[Rh(HS_2Cptn)(cod)]$ (**5**) can be accomplished by $[Rh(\mu\text{-}OH)(cod)]_2$ in

dichloromethane to give the dinuclear compound $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**) in good yield (Scheme 3).

The dinuclear formulation of compound **6** has been corroborated by an X-ray diffraction study (Figure 3). In addition, the NMR spectroscopic data of compound **6** closely resemble those of the previously described dinuclear compounds and do not deserve further comments. Compound **5** has been characterized by elemental analysis, mass spectrum and NMR spectroscopy as a mononuclear species containing a mono-deprotonated $Cptn(SH)_2$ ligand with an unusual k^2S,S' coordination mode. The FAB mass spectrum showed the molecular ion at *m/z* 343 together with the ion at *m/z* 554 corresponding to the dinuclear species. This ion most likely results from the recombination of the produced ions because no mononuclear fragments were observed in the FAB mass spectrum of **6**. In contrast with **6**, that is rigid a room temperature, compound **5** is fluxional and the ^1H NMR showed average resonances for the cod protons. Thus, the =CH and $>CH_2$ protons were observed as broad and featureless resonances at δ 4.18 ppm and, 2.39 and 1.93 ppm, respectively. The resonance of the SH proton probably is also broad and seems to be hidden under the resonances of the cod ligand. The resonance of the SH proton probably is also broad and is hidden under the resonances of the cod ligand. The $^{13}C\{^1H\}$ NMR spectrum showed the full equivalence of the =CH and $>CH_2$ carbons which were observed at δ 81.7 ppm (d, $J_{Rh\text{-}C}$ = 11 Hz) and at δ 31.6 ppm. The resonance of the geminal carbon atom in **5** was observed at δ 66.8 ppm and, as expected, is shifted to higher frequency compared to the resonance of $Cptn(SH)_2$ (δ 23.6 ppm). As could be anticipated this effect is more pronounced in compound **6** where this resonance was observed at δ 81.9 ppm and is the result of the (1:2k^2S, 1:2k^2S´) coordination mode of the doubly deprotonated $Cptn(SH)_2$ ligand.

The spectroscopic information obtained for compound $[Rh(HS_2Cptn)(cod)]$ (**5**) strongly suggest the existence of a dynamic behavior responsible for the chemical equivalence of the =CH protons and carbons of the cod ligand. Assuming a planar or a dynamic puckering four-membered metallacycle,[35] the intramolecular shift of the SH proton between both S-donor atoms together with

the inversion of the sulfur atom bearing the mercapto group would account for the spectroscopic observations. A comparable dynamic process involving the $Au(PPh_3)^+$ fragment, that is isolobal with H^+, has been observed in the early-late heterotrimetallic compound $[Cp^{tt}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\{Au(PPh_3)\}]$ that contain a $[Zr(\mu\text{-}S)_2Ir]$ core.[36]

Molecular structures of $[Rh_2(\mu\text{-}S_2CBn_2)(cod)_2]$ (1), $[Rh_2(\mu\text{-}S_2C^iPr_2)(cod)_2]$ (2), $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (6). The molecular structures of complexes **1**, **2** and **6** are shown in Figures 1, 2 and 3 respectively, and their selected bond lengths and angles are all deliberately arranged in Table 1. In all the three complexes two 'Rh(cod)' moieties are connected through a *gem*-dithiolato $\mu\text{-}S_2CR_2$ double bridge, with the sulfur atoms showing a ($1{:}2k^2S$, $1{:}2k^2S'$) coordination mode. The major differences among the three molecular structures merely concern the distinct *R* substituents of the dithiolato ligands: two benzyl groups in **1**, two *iso*-propyl substituents in **2** and a cyclic 4-membered saturated ring of carbon atoms in **6**.

The coordination geometry around the rhodium centers is in all cases distorted square-planar; the distortions fundamentally arise from the chelating behavior of the two ligands, cod and $\mu\text{-}S_2CR_2$, with the S(1)-Rh-S(2) bond angles in the range 70.40(4)-72.017(13)º, and the inter-olefinic angles (between midpoints of coordinated double bonds) in the range 87.44(16)-88.31(5)º (see table 1). The dihedral angle between the two metal coordination planes are rather similar (91.32(6) (**1**), 92.75(3) (**2**) and 93.59(2)º (**6**)) and the metal-metal separations are almost unaffected by the change in the thiolate substituent (2.8544(5) in **1**, 2.8674(3) in **2**, and 2.8608(2)Å in **6**). As previously observed for other thiolate bridged Rh(I) complexes, both rhodium atoms are slightly displaced out of the coordination mean-plane towards the external part of the molecule (range 0.0197(4)-0.1263(4)Å), proving the existence of a weak repulsion between the metal atoms, most likely due to the ligand-forced short metal-metal nonbonding distance;[23d, 25f, 26] this fact could be also substantiated by the values of the torsion angle Rh(1)-S(1)···S(2)-Rh(2) (94.51(4) in **1**, 96.50(2) in **2**, and 96.22(1)º in **6**))

that, in all cases, are slightly larger (around 3º) than the dihedral angle between coordination planes (see above).

If compared with other related (μ-SR)$_2$ or (μ-SRS) dithiolato complexes, the presence of these *gem*-dithiolato ligands originates a feeble augment of the Rh-S-Rh bond angle (mean 74.12(1)º), but a significant decrease in the S-Rh-S bond angles (71.30(1)º); thus, values reported for closely related dinuclear dithiolato complexes [Rh$_2$(μ-SR)$_2$(cod)$_2$] are (Rh-S-Rh and S-Rh-S mean values, respectively): 77.75 and 75.90º (R = Me),[37] 75.68 and 88.83º (R = C_6F_5),[38] 76.32 and 87.37º (R = $C_6F_4CF_3$),[39] or 74.99 and 79.01° (R_2 = -CH_2CH_2-),[23d] respectively. These structural modifications – fundamentally those affecting the S-Rh-S bond angles– are also coupled with changes in the dihedral angles between the metal coordination planes (as evidenced by the RhS_2Rh torsion angles: 105.49º (R = Me),[37] 118.37º (R = C_6F_5),[38] 117.39 (R = $C_6F_4CF_3$),[39] or 104.16º (R_2 = -CH_2CH_2-)[23d]) and by the existence of shorter intermetallic distances.

All the cycloocta-1,5-diene molecules in **1**, **2** and **6** exhibit the classical *tub* conformation, showing analogous Rh-C and olefinic C-C bond distances to those observed in the above referred dithiolato complexes, reflecting the electronic similarities between *gem* and general dithiolato ligands. Also the Rh-S bond distances observed (Table 1) are in the central region of the separations detected in related dinuclear dithiolato complexes [Rh$_2$(μ-SR)$_2$(cod)$_2$] (range 2.289-2.487, mean 2.38(3) Å).[40]

Synthesis and Characterization of Carbonyl *gem*-Dithiolato-bridged Rhodium Dinuclear Compounds. The dinuclear framework of the *gem*-dithiolato-bridged rhodium compounds is sustained in carbonylation reactions. The carbonylation of the diolefin rhodium compounds **1**, **2** and **6** at room temperature in dichloromethane afforded colored solutions of the corresponding tetracarbonyl complexes [Rh$_2$(μ-S_2CBn_2)(CO)$_4$] (**7**), [Rh$_2$(μ-$S_2C^iPr_2$)(CO)$_4$] (**8**) and [Rh$_2$(μ-S_2Cptn)(CO)$_4$] (**9**). However, the presence of cod in the reaction media, the partial reversibility of the carbonylation processes and the relative instability of these complexes make difficult their isolation.

Attempts to prepare the carbonyl complexes directly from *gem*-dithiol compounds using carbonyl starting materials, as for example $[Rh(acac)(CO)_2]$, were unsuccesfull. Fortunately, the low solubility of compound $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) in n-hexane allowed their isolation under a carbon monoxide atmosphere as a red microcrystalline solid in excellent yield. The dinuclear formulation of **7** relies on the FAB+ spectra that showed the molecular ion at *m/z* 576, and the ions resulting from the sequential losses of four carbonyl ligands. The ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ were in agreement with a C_{2v} symmetry structure resulting from the replacement of a cod ligand by two carbonyls on each rhodium centre. Thus, the equivalent carbonyl ligands were observed as a doublet at δ 184.4 ppm ($J_{Rh\text{-}C}$ = 72 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, and the benzylic protons of the *gem*-dithiolato ligand as a sharp singlet at δ 3.31 ppm in the ^1H NMR spectrum.

The IR spectrum of **7** in solution (CH_2Cl_2) showed three ν(CO) bands for the terminal carbonyl groups at 2078 (m), 2054 (s) and 2010 (s) cm^{-1}. The same pattern has also been observed in the IR of the *in situ* generated solutions of the complexes $[Rh_2(\mu\text{-}S_2C^iPr_2)(CO)_4]$ (**8**) and $[Rh_2(\mu\text{-}S_2Cptn)(CO)_4]$ (**9**) and $[Rh_2(\mu\text{-}S_2Chxn)(CO)_4]$[26] (Table 2) indicating that the formation of dinuclear tetracarbonyl complexes from the parent olefin complexes is clean and quantitative. The observed pattern of intensities (m, s, s) is typical for tetracarbonyl dinuclear complexes having both thiolato and dithiolato bridging ligands.[21a, 24d, 41]

Replacement Reactions on $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ by P-donor Ligands. The carbonyl replacement reactions by P-donor ligands on the complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ takes place quickly at room temperature and stops at the disubstituted complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$ in the case of phosphine ligands (PR'_3 = PPh_3 or PCy_3). Thus, the addition of 2 mol equiv of PPh_3 to solutions of the tetracarbonyl complexes **7** and **8**, generated *in situ* by carbonylation of the corresponding diolefin complexes, afforded orange solutions of the complexes $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(PPh_3)_2]$ (**10**) and $[Rh_2(\mu\text{-}S_2C^iPr_2)(CO)_2(PPh_3)_2]$ (**11**) which were isolated as orange-red

solids in excellent yields. Compound **10** can be alternatively prepared in similar yield by reaction of $Bn_2C(SH)_2$ with [Rh(acac)(CO)(PPh_3)] (1:2 molar ratio) (Scheme 4). This synthetic approach is also the more convenient for the synthesis of the complexes [Rh_2(μ-S_2Cptn)$(CO)_2(PPh_3)_2$] (**12**) and [Rh_2(μ-S_2CBn_2)$(CO)_2(PCy_3)_2$] (**13**) which were obtained as orange and yellow microcrystalline solids in good yield straightforwardly from the corresponding *gem*-dithiol and the appropriate [Rh(acac)(CO)(PR'$_3$)] complexes. The dinuclear formulation of complexes **10**-**13** relies on the FAB + spectra, which showed the molecular ions and the sequential losses of two carbonyl ligands. The complexes exist as the *trans* isomer (C_2 symmetry) although small amounts of the *cis* isomer (C_s symmetry) (< 3%) were observed in the $^{31}P\{^1H\}$ NMR spectra of those complexes containing the less steric demanding PPh_3 ligands (**10**-**12**). The *trans* isomer showed a distinctive complex resonance in the $^{31}P\{^1H\}$ NMR spectra corresponding to an AA'XX' spin system (Figure 4).[42] The observed signals correlate well with the calculated spectra using the parameters reported in Table 3. Interestingly, each phosphorus atom is coupled to both rhodium atoms with a standard $J_{Rh\text{-}P}$ and a negative small $^2J_{Rh\text{-}P}$ coupling constants. In addition, the observed $^3J_{P\text{-}P}$ (≈ 6 Hz) and $J_{Rh\text{-}Rh}$ (3-4 Hz) coupling constants are in good agreement with a *trans* disposition of the PR'$_3$ ligands and the expected short rhodium-rhodium bond distances in the dinuclear complexes. Salient features in the ^1H NMR of compounds **10** and **13** is the AB quartet (J_{AB} ≈ 14 Hz) corresponding to the diastereotopic >CH_2 protons of the benzylic fragment in agreement with the C_2 symmetry of the compounds. Similarly, two doublet resonances were observed for the diastereotopic methyl groups of the isopropyl fragments in complex **11**. The equivalent carbonyl ligands in compounds **10**-**13** were observed as a doublet of doublets (dd) resonance in the $^{13}C\{^1H\}$ NMR spectra with $J_{Rh\text{-}C}$ and $^2J_{P\text{-}C}$ couplings of ≈ 75 and 18 Hz, respectively. Further evidence for the *trans* disposition of the CO ligands in the structures comes from the observation of a strong ν(CO) absorption in the IR of the complexes in solution.[41b, 43]

In contrast with complexes **10**-**13** which do not react further with PR'_3 (PPh_3 or PCy_3), the reaction of complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ with phosphite ligands, $P(OMe)_3$ and $P(OPh)_3$, goes further. The reaction of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) with $P(OMe)_3$ has been studied in detail by $^{31}P\{^1H\}$ NMR (C_6D_6) and four species $[Rh_2(\mu\text{-}S_2CR_2)(CO)_{4-n}\{P(OR)_3\}_n]$ (**Pn**, n = 1, 4) resulting from the partial or total replacement of the CO ligands species have been identified depending on the $P(OR)_3/[Rh_2]$ molar ratio (Table 4). The reaction of **7** with 1 mol equiv of $P(OMe)_3$ gave both the mono- and the disubstituted complexes, **P1** and **P2**. Interestingly, the reaction with 2 mol equiv of $P(OMe)_3$ gave predominantly the disubstituted complex **P2** (mainly the *trans* isomer) although a small amount of the monosubstituted complex **P1** was still observed (figure 5). Increasing the $P(OR)_3$/**7** molar ratio to 3.5 resulted in the formation almost exclusively of **P3** and **P4** (Figure 6). The molecular ions of both species have been detected in the FAB+ spectrum of the resulting solution at *m/z* 836 (**P3**) and 960 (**P4**), respectively. Interestingly, the integrity of the dinuclear unit is preserved when the $P(OR)_3$/**7** molar ratio was further increased since the formation of the cationic mononuclear species $[Rh\{P(OMe)_3\}_4]^+$ was not detected.[44]

The attempt of isolation of **P4** in the solid state was unsuccessful since the compound was obtained as a yellow-orange oil. However, the no formation of **P3** when the $P(OR)_3$/**7** molar ratio was adjusted to 2 suggests that the isolation of the **P2** complexes could be possible. In fact, the complexes $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OMe)_3\}_2]$ (**14**) and $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OPh)_3\}_2]$ (**15**) have been obtained as light orange and yellow solids, respectively, in excellent yield. Both complexes have been fully characterized by elemental analysis, FAB+ mass spectra, and NMR. The $^{31}P\{^1H\}$ NMR spectra showed that the compounds exist mainly as the *trans* isomer although the *cis* isomer is also present in less than 5%. The resonance of the *trans* isomer of both complexes closely resembles those of the related phosphine complexes **10**-**13** and has been simulated with the same AA'XX' spin system using the parameters of Table 3. Noteworthy, similar $^2J_{Rh\text{-}P}$ and $J_{Rh\text{-}Rh}$ but larger $^3J_{P\text{-}P}$ ($\approx$ 15 Hz) coupling constant have been observed.

In contrast with monodentate P-donor ligands, that mainly give rise to *trans* disubstituted complexes, the replacement reactions on $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) using diphosphines with large bite angle, as for example dppp (1,3-bis(diphenylphosphino)propane) or dppb (1,4-bis(diphenylphosphino)butane), resulted in the formation of *cis* disubstituted complexes. The reaction of **7** with 1 mol equiv of dppb gave a yellow solution of the compound $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})]$ (**16**) which was isolated as a yellow solid in good yield. The structure of **16** has been determined by X-ray diffraction methods and is shown in Figure 7. The spectroscopic data obtained from the IR and NMR are in agreement with an approximate C_s molecular symmetry as a result of the coordination of the diphosphine in a *cis* fashion. The diastereotopic $>CH_2$ protons of the benzyl groups of the bridging *gem*-dithiolato ligand are isochronus in C_6D_6 and gave a single resonance at δ 3.94 ppm in the ^1H NMR spectrum. However, the spectrum in $CDCl_3$ showed the expected AB quarted centered at δ 3.56 ppm ($J_{AB} \approx 14$ Hz). The $^{31}P\{^1H\}$ NMR spectrum features a slightly broad doublet with no fine structure centered at δ 32.25 ppm ($J_{Rh\text{-}P} = 157$ Hz). Finally, the equivalent carbonyl ligands were observed as a broad absorption at 1980 cm^{-1} in the IR spectrum in dichloromethane.

The related compound $[Rh_2(\mu\text{-}Bn_2CS_2)(CO)_2(\mu\text{-dppp})]$ has also been identified in the reaction of **7** with dppp (δ 27.87 ppm, d, $J_{Rh\text{-}P} = 170$ Hz) together with other minor unidentified species that could not be easily separated by recrystallization. However, the observed $J_{Rh\text{-}P}$ coupling constants for these species (170-150 Hz) ruled out the formation of cationic compounds as $[Rh(dppp)_2]^+$ or $[Rh(CO)(dppp)_2]^+$, potential products of the degradation of the dinuclear structure.[45]

Molecular Structure of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})]$ (16). A molecular diagram of this dinuclear complex is shown in Figure 7, and key bond lengths and angles are collected in Table 5. Like its diolefin analogues **1**, **2** and **6**, complex **16** shows a folded Rh_2S_2 core, with both Rh atoms in a distorted square-planar coordination. The greatest distortions from this square-planar geometry consist of the small S-Rh-S bond angles (71.047(16) and 71.248(16)º), although the sums of the four

bond angles between pairs of *cis* ligands around each metal add well up to 360.0º. The dihedral angle between the metal coordination planes is significantly larger (99.66(2)º) than those observed in the diolefinic analogues **1**, **2** and **6** (range 91.32(6)-93.59(2)º); according with this fact, the intermetallic separation elongates to 2.9514(3) Å. In this case, there are not structural features that could be indicative of an intermetallic repulsion, as the RhSSRh torsion angle detected is very similar (98.60(2)º) to the inter-planar angle between metal coordination planes.

The diphosphine ligand also bridges the two metals in **16** occupying relative *cisoidal* positions. Interestingly, within both metal coordination planes the larger *cis* angles are those between the dithiolato (S(2)) and the carbonyl groups (101.30(6) and 98.92(6)º), most probably as a subtle consequence of the bridging behavior of the diphosphine ligand in the other side of the metal coordination. The whole structure resembles quite well that of the dithiolato complex [Rh_2(μ-$S^tBu)_2(CO)_2$(μ-dppb)], in which two monodentate *tert*-butyl thiolate groups bridge the two metals of an identical '$Rh_2(CO)_2$(μ-dppb)' moiety.[46]

It could be consider that the *cis* disposition of carbonyl groups is a consequence of the bidentate nature of the dppb ligand. However, a detailed search on related structurally characterized dithiolato analogues, of general stoichiometry [Rh_2(μ-$SR)_2(CO)_2(PR'_3)_2$], reveals that these dithiolato bridged Rh(I) systems exhibit a preference towards a *cis* disposition of the carbonyl groups, not only when the phosphine ligands could restrict the molecular geometry (bidentate phosphines),[46, 47] but also when the PR_3 is monodentate and no geometric restrictions could be envisaged (these are the cases of [Rh_2(μ-$SPy^tBu)_2(CO)_2(PPh_3)_2$],[21a] [$Rh_2$(μ-$S^tBu)_2(CO)_2(PPh_3)_2$],[48] [$Rh_2${μ-$SC_6H_2(^iPr)_3$}$_2(CO)_2$ $(PPh_3)_2$],[49] [Rh_2(μ-$SPh)_2(CO)_2(PMe_3)_2$],[50] or [Rh_2(μ-$S^tBu)_2(CO)_2(PPh_2CH_2CH_2NMe_3)_2$].[51]

As for the Rh-S bond distances, those *trans* to the CO ligands (2.3995 and 2.4001(5) Å) are slightly longer than those *trans* to the phosphines (2.3926 and 2.3801(5) Å), a phenomenon previously descibed in other dithiolato complexes.[21a, 50] The rest of metrical parameters, both in the

metal environments and within the ligands, are very similar to those of literature complexes that have been structurally characterized.[21a, 48-51]

Discussion

The synthesis of dinuclear $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (M = Rh, Ir) complexes can be accomplished by direct deprotonation of *gem*-dithiol compounds with rhodium or iridium complexes that contain basic ligands. The diolefin complexes $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (M = Rh, Ir) are accessible from the dinuclear complexes $[M(\mu\text{-}OH)(cod)]_2$ and $[M(\mu\text{-}OMe)(cod)]_2$, or the mononuclear [M(acac)(cod)], sometimes in the presence of an external base. The dinuclear complexes are generally obtained in high yield although, in the case of $^{i}Pr_2C(SH)_2$, the syntheses are complicated by the formation of the trinuclear hydride clusters $[M_3(\mu_3\text{-}S)_2(\mu\text{-}H)(cod)_3]$[33] which can be easily separated by chromatography. The formation of the sulfido clusters resulted from the SH_2(g) produced in the decomposition of $^{i}Pr_2C(SH)_2$ as has been evidenced by the detection of $^{i}Pr_2C$=S by GC/MS. The stepwise deprotonation of the *gem*-dithiol compounds has only been observed in the case of $Cptn(SH)_2$ and both, the mononuclear $[Rh(HS_2Cptn)(cod)]$ (**5**) and the dinuclear $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**) compounds, have been isolated and fully characterized.

This synthetic methodology is also applicable to the preparation of the complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$, which can be also prepared from $[Rh(acac)(CO)(PR'_3)]$ (R' = Ph, Cy), but not to the carbonyl complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$. However, these complexes have been obtained by carbonylation of the corresponding diolefin compounds and are precursors for the disubstituted complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$ after carbonyl replacement by P-donor ligands (R' = Ph, Cy, OMe, OPh).

The above described results on the synthesis of *gem*-dithiolato-bridged complexes $[Rh_2(\mu\text{-}S_2CR_2)(L_2)_2]$ are, in some aspects, comparable to those previously described in bis-thiolato, $[Rh(\mu\text{-}SR)(L_2)]_2$, or dithiolato, $[Rh_2(\mu\text{-}S(CH_2)_nS)(L_2)_2]$ (n = 2 - 4), complexes as they all have an open-book

structure. However, significant differences are observed in nuclearity, stereochemistry and reactivity that are probably a consequence of the special geometrical constrains imparted by the *gem*-dithiolato ligand in the M_2S_2 core. The bridging and chelating coordination mode (1:2κ^2S, 1:2κ^2S´) of the *gem*-dithiolato ligands results in the formation of two four-membered metallocycles. In addition, the presence of a single bridgehead carbon atom between both sulfur atoms produces a compact and rigid M_2S_2 core with a small angle between the coordination planes of the rhodium centers and short metal-metal distances.

The bis-thiolato complexes can exist as different conformers (*syn-exo*, *syn-endo* and *anti*) that arise from the spatial arrangement of the bridging thiolato ligands with a 1:2κ^2S coordination mode.[52] However, a large number of diolefin complexes $[M(\mu\text{-SR})(cod)]_2$ (M = Rh, Ir) display a *syn-endo* conformation in the solid state and have a dynamic behavior by inversion of the non-planar Rh_2S_2 ring.[21a, 41b, 53, 54] In contrast, the dinuclear complexes $[Rh_2(\mu\text{-}S_2CR_2)(cod)_2]$ are static as should be expected by the structure of the bridging ligand that blocks the ring-flipping process. On the other hand, dithiolato ligands afforded di- or tetranuclear complexes depending on the structure of the dithiolato ligand. For example, the nuclearity of the rhodium complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(cod)_2]_x$ is influenced by the number of methylenic units between the two sulfur atoms. Thus, dinuclear complexes (x = 1) were prepared for n = 2, 3 but a tetranuclear complex was obtained in the case of 1,4-butanedithiolato ligand (n = 4).[23d] More sophisticated ligands, as for example, 1,1'-binaphthalene-2,2'-dithiolato, gave a mixture of both di- and tetranuclear complexes.[24e] Interestingly, the tetranuclear complexes were easily converted to dinuclear complexes by carbonylation at atmospheric pressure, i.e. $[Rh_2(\mu\text{-}S(CH_2)_4S)(CO)_4]$, indicating the strong influence of the auxiliary ligands on the nuclearity.[23d] Similarly, dinuclear complexes $[Rh(\mu\text{-SR})_2(CO)_2]_2$ and $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ were obtained along the carbonyl series with bis-thiolato and *gem*-dithiolato ligands, respectively.

The replacement reactions by monodentate P-donor ligands on the tetracarbonyl complexes, usually stops at the disubstituted complexes. The solid state structure of the complexes $[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2$ show a *cis* arrangement of the bulky phosphine or phosphite ligands and an *anti* conformation of the bridging thiolato ligands with the *endo* substituent at the side of the molecule with the small carbonyls ligands.[21a,48-51,55] However, in some complexes a dynamic equilibrium between the *cis* and *trans* isomers has been observed in solution.[41b, 43b, 50] In contrast, the complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR_3)_2]$, that do not have any conformational restriction associated to the bridging ligand, exist predominantly as the *trans* isomer. In the dithiolato series, the carbonyl replacement reactions in some dinuclear tetracarbonyl complexes encompass a change of nuclearity and the formation of tetranuclear complexes is quite common depending on the structure of the dithiolato ligand.[23c, 24d-e] Nevertheless, some dinuclear complexes exit exclusively as the *trans* isomer, [23d, 56] although *cis*/*trans* mixtures have been observed in other cases.[23c, 57]. Another striking difference between the three types of complexes concerns the formation of pentacoordinated species in the substitution process that evolve to the disubstituted complex by decarbonylation. Thus, the species $[Rh(\mu\text{-}SR)(CO)_2(PR_3)]_2$ have been characterized in the bis-thiolate chemistry[43b] but have not been observed in the *gem*-dithiolato complexes. Interestingly, related species have detected in dithiolate chemistry under CO pressure.[58]

An additional remarkable difference between bis-thiolate and *gem*-dithiolate chemistry concerns the pattern of substitution by monodentate phosphite ligands. As described above, it is possible to replace the four carbonyl ligands in complex $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) as was evidenced by the characterization of the complex $[Rh_2(\mu\text{-}S_2CBn_2)\{P(OMe)_3\}_4]$. However, the disubstituted complex $[Rh(\mu\text{-}S^tBu)(CO)\{P(OMe)_3\}]_2$ does not react further with $P(OMe)_3$ in spite that compound $[Rh(\mu\text{-}S^tBu)\{P(OMe)_3\}_2]_2$ can be prepared from $[Rh(\mu\text{-}Cl)\{P(OMe)_3\}_2]_2$ and LiS^tBu.[59]

As far as the carbonyl replacement by diphosphine ligands is concerned, it is important to notice that a large number of bis-thiolato complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2(\mu\text{-diphos})]$ containing bridging

diphosphine ligands have been characterized as the *cis-anti* isomer.[46, 60] In the same way, replacement reactions on the carbonyl *gem*-dithiolato complexes gives the expected *cis* isomer as has been exemplified by the synthesis of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})]$ (**16**). However, in the dithiolato series the dinuclear framework is not generally preserved as was evidenced by the formation of ion-pair compounds $[Rh(dppp)_2][Rh(dithiolato)(CO)_2]$ as the result of the sequestering of a rhodium atom by dppp.[23b]

Concluding remarks

We have described the high yield synthesis of dinuclear $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (M = Rh, Ir) and $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR_3)_2]$ complexes by double deprotonation of diverse *gem*-dithiol compounds using mono- or dinuclear rhodium complexes containing basic ligands. The diolefin complexes are precursors for the carbonyl complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ which undergo stereoselective replacement reactions by P-donor ligands to give the *trans* disubstituted complexes with monodentate ligands, and the *cis* complexes with bridging diphosphines. The synthetic versatility of this kind of complexes, the singular structural features of the compact Rh_2S_2 core enforced by the *gem*-dithiolato bridging ligand, and the catalytic activity for the hydroformylation of alkenes open the possibility of study of the influence of the *gem*-dithiolato ligand on the catalytic activity. Further studies concerning the reactivity and catalytic activity of these complexes are currently in progress.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complexes **1**, **2**, **6** and **16**. This material is available free of charge via Internet at http://pubs.acs.org.

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Table 1. Selected Bond Distances (Å) and Angles (°) for **1**, **2** and **6**.*

	Complex **1**	Complex **2**	Complex **6**		Complex **1**	Complex **2**	Complex **6**
Rh(1)···Rh(2)	2.8544(5)	2.8674(3)	2.8608(2)				
Rh(1)-S(1)	2.3979(12)	2.3514(5)	2.3690(4)	Rh(2)-S(1)	2.3748(12)	2.3633(6)	2.3627(4)
Rh(1)-S(2)	2.4078(11)	2.3819(6)	2.3896(4)	Rh(2)-S(2)	2.3650(12)	2.3581(5)	2.3618(4)
Rh(1)-C(1)	2.137(5)	2.142(2)	2.1406(15)	Rh(2)-C(9)	2.129(4)	2.126(2)	2.1367(16)
Rh(1)-C(2)	2.142(4)	2.143(2)	2.1449(16)	Rh(2)-C(10)	2.155(4)	2.157(2)	2.1419(16)
Rh(1)-C(5)	2.125(4)	2.119(2)	2.1358(16)	Rh(2)-C(13)	2.129(4)	2.138(2)	2.1411(15)
Rh(1)-C(6)	2.135(5)	2.141(2)	2.1444(16)	Rh(2)-C(14)	2.122(5)	2.135(2)	2.1334(16)
S(1)-C(17)	1.847(4)	1.870(2)	1.8613(16)	S(2)-C(17)	1.867(4)	1.875(2)	1.8640(16)
C(1)-C(2)	1.378(7)	1.392(3)	1.397(2)	C(9)-C(10)	1.387(6)	1.389(3)	1.398(2)
C(5)-C(6)	1.373(7)	1.390(3)	1.400(2)	C(13)-C(14)	1.386(7)	1.394(3)	1.398(2)
C(17)-C(18)	1.541(6)	1.550(3)	1.543(2)	C(17)-C(19)$^{\#}$	1.544(6)	1.559(3)	1.549(2)
S(1)-Rh(1)-S(2)	70.40(4)	71.122(19)	71.420(13)	S(1)-Rh(2)-S(2)	71.53(4)	71.331(19)	72.017(13)
S(1)-Rh(1)-M(1)	172.17(12)	172.95(5)	172.39(4)	S(1)-Rh(2)-M(3)	170.81(12)	170.87(5)	172.33(4)
S(1)-Rh(1)-M(2)	100.14(12)	98.73(5)	99.10(4)	S(1)-Rh(2)-M(4)	99.51(12)	99.91(5)	99.70(4)
S(2)-Rh(1)-M(1)	101.83(11)	102.07(5)	101.11(4)	S(2)-Rh(2)-M(3)	100.75(11)	100.67(5)	100.46(3)
S(2)-Rh(1)-M(2)	170.49(11)	169.21(5)	170.33(4)	S(2)-Rh(2)-M(4)	168.36(11)	170.89(5)	169.28(3)
M(1)-Rh(1)-M(2)	87.61(15)	87.94(7)	88.31(5)	M(3)-Rh(2)-M(4)	87.44(16)	87.85(7)	87.95(5)
Rh(1)-S(1)-Rh(2)	73.46(3)	74.916(17)	74.399(12)	Rh(1)-S(2)-Rh(2)	73.45(3)	74.445(16)	74.038(12)
Rh(1)-S(1)-C(17)	84.55(13)	86.65(7)	84.66(5)	Rh(1)-S(2)-C(17)	83.85(13)	85.66(7)	84.02(5)
Rh(2)-S(1)-C(17)	88.23(13)	86.80(7)	86.86(5)	Rh(2)-S(2)-C(17)	88.06(14)	86.84(7)	86.83(5)
S(1)-C(17)-S(2)	96.47(19)	94.65(10)	96.42(7)	C(18)-C(17)-C(19)$^{\#}$	108.5(3)	111.23(17)	105.48(13)
S(1)-C(17)-C(18)	113.4(3)	110.12(14)	112.84(11)	S(2)-C(17)-C(18)	109.4(3)	110.03(14)	113.49(11)
S(1)-C(17)-C(19)$^{\#}$	115.4(3)	114.61(14)	115.42(11)	S(2)-C(17)-C(19)$^{\#}$	113.2(3)	115.12(15)	113.41(11)

* M(1), M(2), M(3) and M(4) represent the midpoints of the olefinic C(1)-C(2), C(5)-C(6), C(9)-C(10) and C(13)-C(14) bonds. $^{\#}$ In complex **6,** the atom label of carbon atom bonded to C(17), analogous to C(19) in **1** and **2**, corresponds to C(21).

Table 2. ν(CO) Stretching Frequencies (cm^{-1}) observed in the IR Spectra in Solution (CH_2Cl_2) of the Carbonyl Complexes **7**-**9**

Complex	ν (CO)	Colour
$[Rh_2(\mu\text{-}S_2Chxn)(CO)_4]$[a]	2082 (m), 2058 (s), 2013 (s) cm^{-1}	red-brown
$[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**)	2078 (m), 2054 (s), 2010 (s) cm^{-1}	red
$[Rh_2(\mu\text{-}S_2C^iPr_2)(CO)_4]$ (**8**)	2080 (m), 2055 (s), 2011 (s) cm^{-1}	yellow-brown
$[Rh_2(\mu\text{-}S_2Cptn)(CO)_4]$ (**9**)	2082 (m), 2059 (s), 2014 (s) cm^{-1}	yellow-brown

[a] Reference 26.

Table 3. $^{31}P\{^{1}H\}$ NMR (121.47 MHz, 293 K) Data for the Compounds $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$[a]

Compound	isomer	δ	$J_{Rh\text{-}P}$	$^{2}J_{Rh\text{-}P}$	$^{3}J_{P\text{-}P}$	$J_{Rh\text{-}Rh}$
$[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(PPh_3)_2]$ (**10**)[b]	*trans*	41.59	163.70	- 1.46	6.22	3.12
	cis	39.60	163			
$[Rh_2(\mu\text{-}S_2C^{i}Pr_2)(CO)_2(PPh_3)_2]$ (**11**)[b]	*trans*	41.76	163.10	- 1.80	6.45	3.42
	cis	40.20	163			
$[Rh_2(\mu\text{-}S_2Cptn)(CO)_2(PPh_3)_2]$ (**12**)[c]	*trans*	41.37	163.50	- 1.23	6.19	3.58
	cis	39.00	162			
$[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(PCy_3)_2]$ (**13**)[c]	*trans*	51.56	156.88	- 0.76	4.29	3.33
$[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OMe)_3\}_2]$ (**14**)[b]	*trans*	139.96	258.07	-1.95	14.00	2.89
	cis	141.00	252			
$[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OPh)_3\}_2]$ (**15**)[c]	*trans*	122.08	276.82	- 2.00	15.94	2.63
	cis	123.30	273			

[a] The data of the *trans* isomers correspond to the calculated spectrum: AA'XX' spin system, A = ^{31}P and X = ^{103}Rh (δ in ppm and *J* in Hz). [b] In C_6D_6. [c] In $CDCl_3$.

Table 4. $^{31}P\{^{1}H\}$ NMR Data (C_6D_6) for the **Pn** Compounds $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_{4-n}\{P(OMe)_3\}_n]$ (**n** denotes the number of $P(OMe)_3$ ligands in the dinuclear framework)[a]

Compound	δ (ppm)	*J* (Hz)
P1	138.7	$J_{Rh\text{-}P} = 256$
P2[c]	139.96 (*trans* isomer)[b]	$J_{Rh\text{-}P} = 258.07$, $^{2}J_{Rh\text{-}P} = -1.95$, $^{3}J_{P\text{-}P} = 14.0$, $J_{Rh\text{-}Rh} = 2.89$
	141.0 (*cis* isomer)	$J_{Rh\text{-}P} = 252$
P3[b]	146.1 (P_a), 145.3 (P_b), 142.2 (P_c)	$J_{Rh1\text{-}Pa} = 275$, $J_{Rh2\text{-}Pb} = 275$, $J_{Rh2\text{-}Pc} = 258$, $J_{Pb\text{-}Pc} = 10.4$, $J_{Pa\text{-}Pc} = 3$
P4	146.6	$J_{Rh\text{-}P} = 272$

[a] For the labeling scheme used in P3 see figure 6. [b] Calculated spectrum. [c] P2 is actually compound **14**.

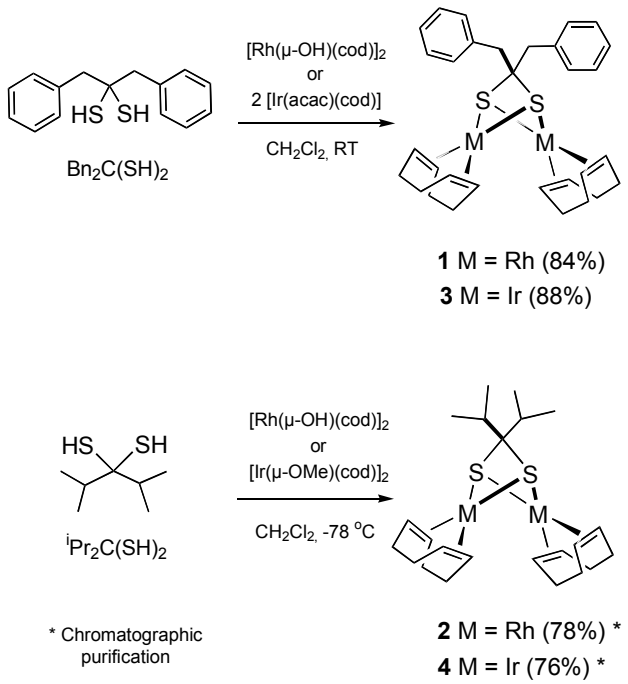
Table 5. Selected Bond Distances (Å) and Angles (°) for **16**

Rh(1)-S(1)	2.3995(5)	Rh(2)-S(1)	2.4001(5)
Rh(1)-S(2)	2.3926(5)	Rh(2)-S(2)	2.3801(5)
Rh(1)-P(1)	2.2655(5)	Rh(2)-P(2)	2.2618(5)
Rh(1)-C(1)	1.840(2)	Rh(2)-C(2)	1.837(2)
S(1)-C(3)	1.869(2)	S(2)-C(3)	1.867(2)
P(1)-C(21)	1.851(2)	P(2)-C(18)	1.834(2)
P(1)-C(22)	1.830(2)	P(2)-C(34)	1.819(2)
P(1)-C(28)	1.823(2)	P(2)-C(40)	1.826(2)
C(1)-O(1)	1.142(2)	C(2)-O(2)	1.144(3)
C(3)-C(4)	1.540(3)	C(3)-C(11)	1.551(3)
C(18)-C(19)	1.536(3)	C(19)-C(20)	1.531(3)
C(20)-C(21)	1.528(3)		
S(1)-Rh(1)-S(2)	71.047(16)	S(1)-Rh(2)-S(2)	71.248(16)
S(1)-Rh(1)-P(1)	96.810(17)	S(1)-Rh(2)-P(2)	95.385(18)
S(1)-Rh(1)-C(1)	172.34(6)	S(1)-Rh(2)-C(2)	168.50(6)
S(2)-Rh(1)-P(1)	166.816(18)	S(2)-Rh(2)-P(2)	166.080(18)
S(2)-Rh(1)-C(1)	101.30(6)	S(2)-Rh(2)-C(2)	98.92(6)
P(1)-Rh(1)-C(1)	90.82(6)	P(2)-Rh(2)-C(2)	94.77(6)
Rh(1)-S(1)-Rh(2)	75.894(15)	Rh(1)-S(2)-Rh(2)	76.399(14)
Rh(1)-S(1)-C(3)	85.21(6)	Rh(1)-S(2)-C(3)	85.46(6)
Rh(2)-S(1)-C(3)	85.19(6)	Rh(2)-S(2)-C(3)	85.82(6)
S(1)-C(3)-S(2)	96.36(9)	C(4)-C(3)-C(11)	112.35(16)
S(1)-C(3)-C(4)	110.01(13)	S(2)-C(3)-C(4)	113.87(13)
S(1)-C(3)-C(11)	112.95(14)	S(2)-C(3)-C(11)	110.36(13)
Rh(1)-C(1)-O(1)	179.6(2)	Rh(2)-C(2)-O(2)	176.16(19)

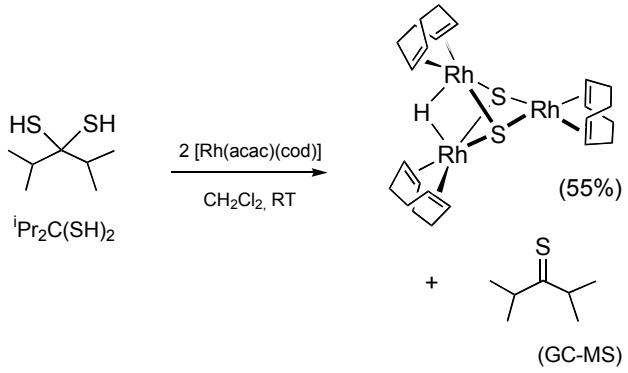
Table 6. Crystal Data, Data Collection and Refinement Parameters for Complexes **1**, **2**, **6** and **16.**

complex	**1**	**2**	**6**	**16**
empirical formula	$C_{31}H_{38}Rh_2S_2$	$C_{23}H_{38}Rh_2S_2$	$C_{21}H_{32}Rh_2S_2$	$C_{45}H_{42}O_2P_2Rh_2S_2 \cdot CH_2Cl_2$
crystal size, mm	0.17 x 0.09 x 0.06	0.38 x 0.11 x 0.02	0.34 x 0.34 x 0.34	0.37 x 0.23 x 0.22
fw	680.55	584.47	554.41	1031.59
space group	$P2_1/n$ (No. 14)	P-1 (No. 2)	P-1 (No. 2)	$P2_1/n$ (No. 14)
a, Å	6.3798(5)	6.4559(4)	7.5580(5)	17.6034(12)
b, Å	20.1991(16)	10.8020(6)	9.9802(6)	10.6870(7)
c, Å	21.1670(17)	16.8466(10)	15.1423(9)	24.2161(17)
α, °	90.0	99.427(1)	108.7250(10)	90.0
β, °	97.660(2)	91.151(1)	92.1170(10)	107.7410(10)
γ, °	90.0	104.990(1)	108.5870(10)	90.0
V, Å ^{3} / Z	2703.4(4) / 4	1117.11(11) / 2	1012.90(11) / 2	4339.1(5) / 4
D_{calcd}, g·cm^{-3}	1.672	1.738	1.818	1.579
μ, mm^{-1}	1.394	1.671	1.837	1.092
min. max. transm. factors	0.787, 0.919	0.566, 0.964	0.537, 0.542	0.685, 0.792
no. of measd. reflns	17795 ($1.40 \leq \theta \leq 28.61$)	13859 ($1.98 \leq \theta \leq 28.34$)	12332 ($2.24 \leq \theta \leq 28.29$)	51934 ($1.71 \leq \theta \leq 28.31$)
no. of unique reflns	6347 ($R_{int} = 0.1029$)	5274 ($R_{int} = 0.0252$)	4718 ($R_{int} = 0.0132$)	10466 ($R_{int} = 0.0286$)
no. data/restraints/param	6347/0/324	5274/0/396	4718/0/354	10466/0/681
GOF(all data)[a]	0.927	1.026	1.103	1.056
$R_1(F)$ (only for $F^2 > 2\sigma(F^2)$)[b]	0.0487 (4572 refl.)	0.0231 (4699 refl.)	0.0160 (4539 refl.)	0.0257 (9397 refl.)
$wR_2(F^2)$ (all data)[c]	0.1005	0.0511	0.0398	0.0603

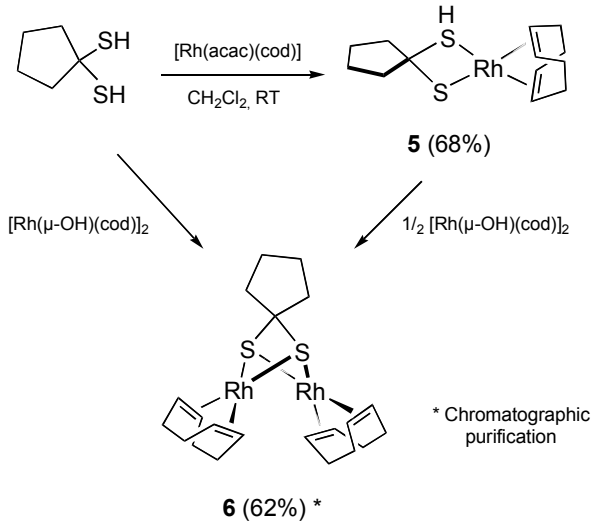
[a] GOF = $(\Sigma[w(F_o^2 - F_c^2)^2] / (n - p))^{1/2}$, where n and p are the number of data and parameters. [b] $R_1(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ only for observed reflections (in parenthesis). [c] $wR_2(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2])^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(0, F_o^2) + 2F_c^2]/3$.



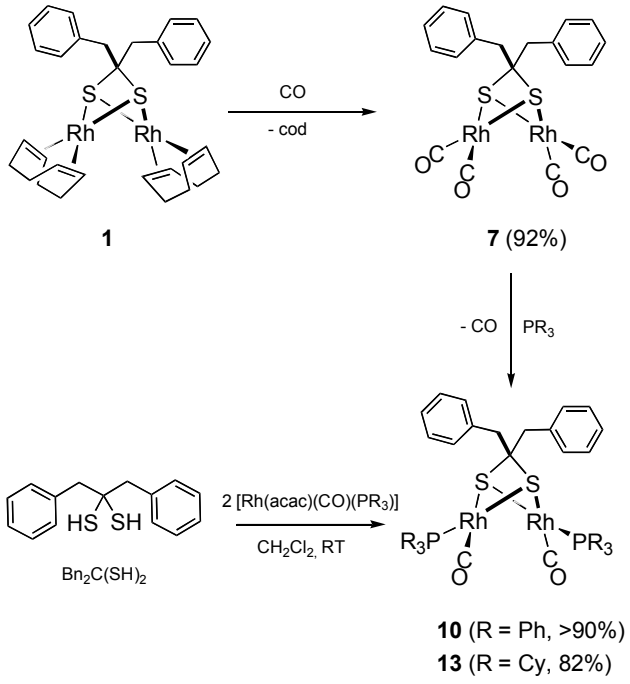
Scheme 1. Synthesis of rhodium and iridium *gem*-dithiolato-bridged dinuclear diolefin complexes



Scheme 2. Formation of a trirhodium hydride cluster by deprotonation of $^{i}Pr_2C(SH)_2$



Scheme 3. Stepwise formation of the *gem*-dithiolato-bridged dinuclear complex **6**



Scheme 4. Replacement reactions on *gem*-dithiolato-bridged dinuclear complexes

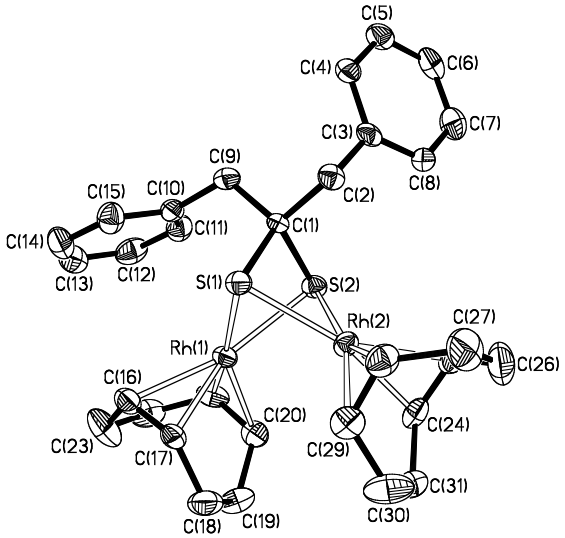


Figure 1. Molecular structure of compound $[Rh_2(\mu\text{-}S_2CBn_2)(cod)_2]$ (**1**)

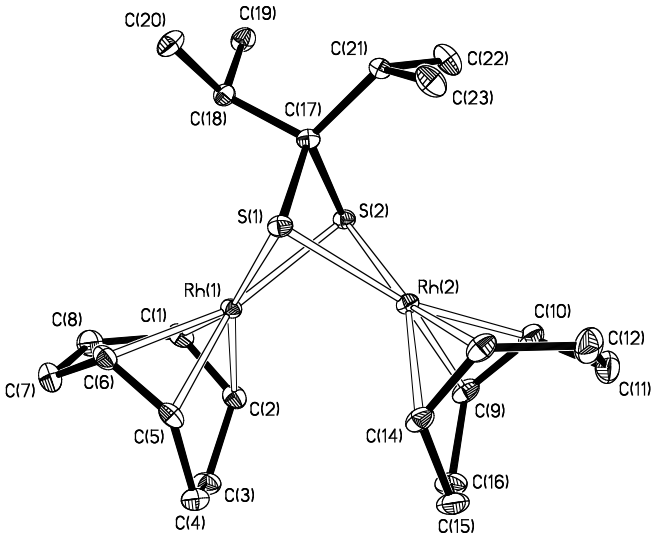


Figure 2. Molecular structure of compound $[Rh_2(\mu\text{-}S_2C^iPr_2)(cod)_2]$ (**2**)

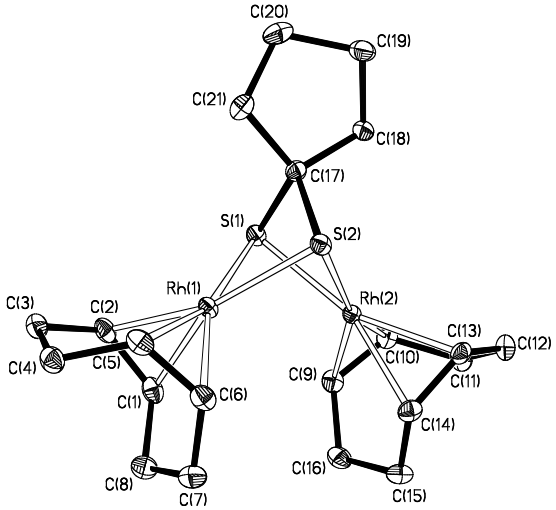


Figure 3. Molecular structure of compound $[Rh_2(\mu\text{-}S_2Cptn)(cod)_2]$ (**6**)

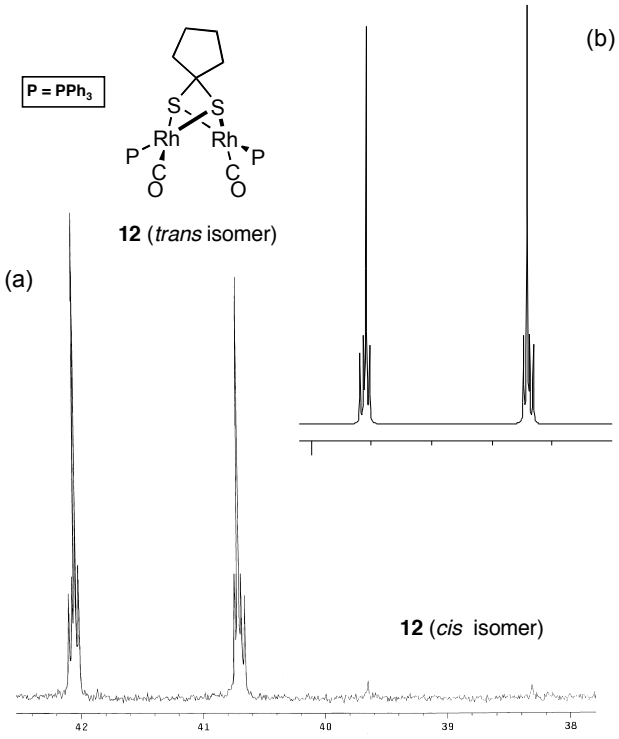


Figure 4. (a) $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) spectrum of $[Rh_2(\mu\text{-}S_2Cptn)(CO)_2(PPh_3)_2]$ (**12**). (b) Calculated $^{31}P\{^1H\}$ NMR spectrum for the AA'XX' spin system observed for the *trans* isomer

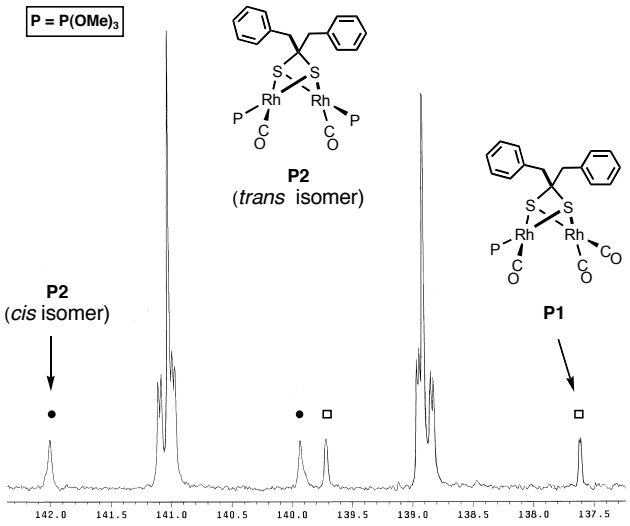


Figure 5. $^{31}P\{^{1}H\}$ NMR (C_6D_6) of the reaction of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) with 2 mol equiv of $P(OMe)_3$ showing exclusively the presence of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2\{P(OMe)_3\}_2]$ (**P2**, *cis* and *trans* isomers, compound **14**) and $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_3\{P(OMe)_3\}]$ (**P1**)

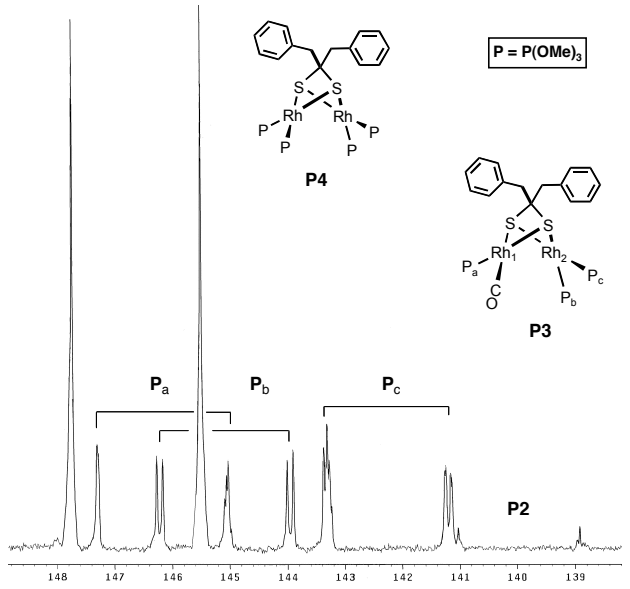


Figure 6. $^{31}P\{^{1}H\}$ NMR (C_6D_6) of the reaction of $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_4]$ (**7**) with 3.5 mol equiv of $P(OMe)_3$ showing the presence of $[Rh_2(\mu\text{-}S_2CBn_2)\{P(OMe)_3\}_4]$ (**P4**), $[Rh_2(\mu\text{-}S_2CBn_2)(CO)\{P(OMe)_3\}_3]$ (**P3**) and traces of **P2**

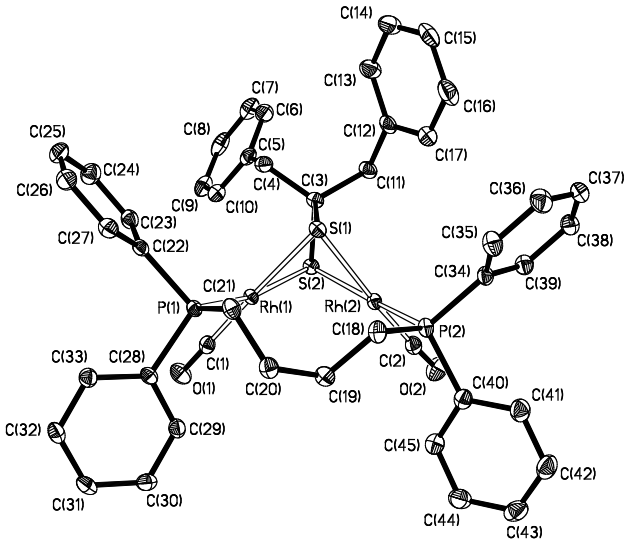


Figure 7. Molecular structure of compound $[Rh_2(\mu\text{-}S_2CBn_2)(CO)_2(\mu\text{-dppb})]$ (**16**)

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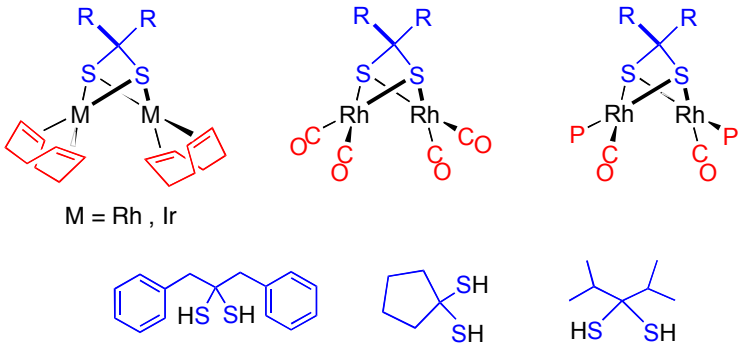

The dinuclear complexes $[M_2(\mu\text{-}S_2CR_2)(cod)_2]$ (M = Rh, Ir) have been straightforwardly obtained by deprotonation of a range of *gem*-dithiol compounds with standard diolefin rhodium and iridium complexes containing basic ligands. The carbonylation of the diolefin compounds gave the complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_4]$ which stereoselectively undergo the carbonyl replacement by P-donor ligands to give the *trans* mixed-ligand disubstituted complexes $[Rh_2(\mu\text{-}S_2CR_2)(CO)_2(PR'_3)_2]$.